

Electron-Sensitive Materials

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Certain additives increase the electron sensitivity of Kodak's negative photoresists by a factor of five to seven; others increase the sensitivity of AZ-1350 by a factor of two to three. With additives the contrast of the negative resists is increased, leading to sharper edges and higher resolution. Some of these additives also increase the light sensitivity of both positive and negative resists. A recording system based on a silver halide emulsion and containing a conductive underlay is also described.

I. INTRODUCTION

An electron beam pattern generator developed at the Western Electric Engineering Research Center requires novel recording systems that possess high resolution, high sensitivity at short exposure times, flat surfaces, and a conductive underlay.¹ Silver halide emulsions are best suited for the generation of reticles by this generator, while for the production of one-to-one masks or the generation of patterns directly onto silicon slices (thereby avoiding the use of masks) photoresists are the preferred recording media.

High-resolution emulsions and photoresists were chosen over other recording media since they offer the best combination of sensitivity and resolution.²⁻¹⁵ (See Table I.) Systems using these two recording media are discussed in this paper.

II. SILVER HALIDE RECORDING MEDIA

Kilovolt electrons passing through silver halide grains form latent images in much the same way as photons.¹⁶ Although electron scattering by the grains causes some loss in resolving power, the edges of lines generated by writing electron beams have been found to be as sharp as edges made by conventional processes.

The recording medium required when the writing beam is used for

TABLE I—ELECTRON BEAM RECORDING MEDIA

Recording Media	Smallest Spot Recorded (μm)	Flux of 15-keV Electrons Needed to Record (C/cm^2)	Ref.
High resolution silver halide emulsion	1-2	10^{-9}	2, 3
Photoresists			
Negative (KPR, KTFR)	0.25	$8-10 \times 10^{-6}$	4, 5
Positive (AZ-1350)	1	6×10^{-6}	6
Methacrylate resists	0.5	8×10^{-6}	7
Silicone resists	0.4	$\sim 10^{-6}$	8, 9
Polymerization of monomers absorbed from the vapor	1.5×10^{-2}	10^{-1}	10
Liquid crystals	30	$\approx 10^{-9}$	11
Ferromagnetics	>100	≈ 1	12, 13
Thermoplastics	≈ 10	$>5 \times 10^{-4}$	14
Electrostatic	>50	N.A.	15

reticle generation is made in the following way: Eastman-Kodak coats a high-resolution emulsion (649-GH) on glass manufactured by Liberty Mirror Company, Brackenridge, Pennsylvania. Seamed $6'' \times 6''$ glass plates, covered with a Liberty Mirror proprietary PE-S1-E conductive coating, transmitting 75-80 percent of incident visible light, are used so that uniform coatings can be obtained. The majority of the transmission loss is in the glass. The surface of the glass is flat to $\pm 27 \mu$ inch per linear inch, which is sufficiently flat so that the total error of ± 20 PPM allowed for the electron beam machine is not exceeded.¹ In order to meet this flatness specification, glass 0.235 ± 0.01 inch thick is used. The plates are cut to $3'' \times 3''$ before they are used in the electron beam pattern generator. A conductive coating is used to avoid charge storage by the recording medium. The proprietary Liberty Mirror coating was chosen since it is highly conductive ($<1000 \Omega/\text{square}$), transparent (optical density <0.04), resistant to the precleaning procedure used by Kodak before coating with emulsion, and can be applied without heating the substrate.

III. ELECTRON RECORDING BY PHOTORESISTS

It is likely that the chemical reactions that the electrons cause in photoresists are the same as those induced by light. Negative resists undergo cross-linking^{17,18} while positive photoresists are usually converted to carboxylic acids¹⁷ and perhaps lactones.¹⁹

The direct exposure of photoresist coatings on the surface of silicon slices appears to be an attractive means of patterning semiconductor

substrates. For this application the exposure time presently required for a writing beam is unacceptably long.¹ Increasing the beam current to reduce exposure times might lead to undesirable thermal effects, so work on increasing the sensitivity of photoresists was initiated. Both positive and negative resists were examined in order that the electron beam pattern generator would never be required to pattern more than half the addressable points, thereby minimizing exposure times.

3.1 *Chemical Additives to Increase the Sensitivity of Negative Photoresists*

Recently, chemical additives have been found here²⁰ which reduce the flux of 15 keV electrons needed to expose negative photoresists from $8\text{--}10 \times 10^{-6}$ C/cm² to 1.5×10^{-6} C/cm². The absorbed energy required for full exposure corresponds to 4.2×10^{20} eV/cm³.¹⁸ Further reductions in the required exposure are anticipated.

The additives, incorporated into the photoresist solution before it is applied, divide into two classes based on their mechanisms. The first class, alkyl and aryl compounds of heavy metals, e.g., hexaphenyldilead, reduce the required flux by acting in two ways: (i) they increase the capture cross section of the resist so that more energy is transferred to the resist layer, and (ii) since these compounds are readily dissociated into free radicals, they probably reduce the required flux by initiating more than the average number of crosslinks. The second class of additives, of which benzophenone is typical, does not increase the capture cross section but does cause more than normal crosslinking. This occurs either because the additives are readily dissociated into free radicals which initiate crosslinking, or because they are excited to low-lying triplet states after the primary process of absorption.^{21,22} These triplet states decay slowly and transfer energy to more distant polymers causing them to crosslink.

Figure 1 shows the typical effects of an additive. The thickness of exposed and developed KTFR is given as a function of the exposing flux, both with and without benzophenone. Note that there is a threshold; that is, no insolubilization occurs below a certain flux of electrons. Since negative resists are a subset of crosslinking systems, they are not insolubilized until there is an average of one crosslink per molecule. Sufficient radiation to form this average number of crosslinks per molecule makes part of the radiated resist insoluble, giving rise to a threshold. Further radiation increases the thickness of the exposed photoresist by insolubilizing more and more of it until the maximum thickness is obtained. Similar results have been found

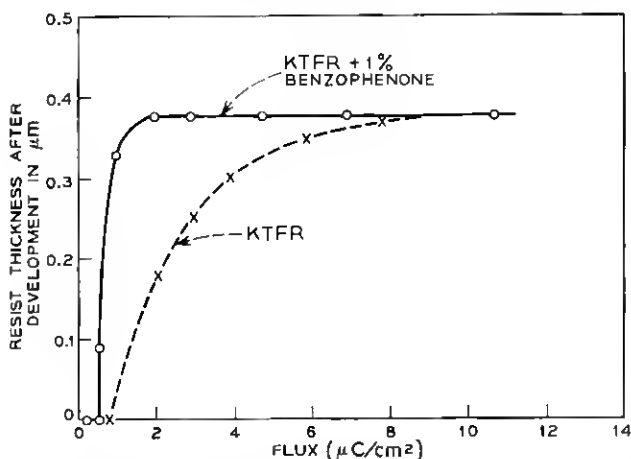


Fig. 1—Effect of benzophenone on the exposure of KTRF by 15 keV electrons. The initial thickness of the resist was $0.6 \mu\text{m}$.

with KPR. Figure 1 also shows that the slope of the photoresist thickness versus flux curve is much higher when additives are present; that is, the resist with additives is a high contrast recording medium.

Γ has been defined here as a contrast function for photoresists. Analogous to γ used in photography to specify the contrast of a film, Γ is defined:

$$\Gamma = \frac{\text{threshold flux}}{\text{flux for maximum thickness}}$$

so that

$$0 < \Gamma \leq 1.$$

A high Γ implies good contrast, giving sharp edges in the patterning process.

Some of the results that have been obtained on increasing both the sensitivity and the contrast of KTRF and KPR are shown in Table II. Although benzophenone and hexaphenyldilead are equally efficacious in reducing the flux required for full exposure, benzophenone is the preferred additive since it is more soluble in photoresists. Benzil and 1,4-diphenyl-1,3-butadiene show behavior quite similar to benzophenone.

3.2 The Electron Exposure of AZ-1350—A Positive Photoresist

The solubility of AZ-1350 films as a function of the exposing flux of 15 keV electrons is shown in Fig. 2. Typical results obtained with

TABLE II—ADDITIVES THAT INCREASE THE SENSITIVITY AND CONTRAST OF NEGATIVE PHOTORESISTS

Resist	Additive	Flux of 15-keV Electrons Needed to Expose ($\mu\text{C}/\text{cm}^2$)	Γ
KTFR	None	8	0.11
	1.0% benzophenone	1.5	0.33
	Hexaphenyldilead (sat.)	1.5	0.33
	2.0% triphenylbismuth	1.9	0.5
KPR	None	10	0.09
	1.0% benzophenone	1.5	0.33

newly purchased AZ-1350 are presented in curves A and B and are summarized below. At low exposures ($<10^{-8}$ C/cm²) no solubilization occurs and no image can be detected in the photoresist. Fluxes between 10^{-8} and about 6×10^{-6} C/cm² cause an image to form after development; some of the resist is solubilized, but not all can be removed. If the irradiation is brought up to fluxes between 6×10^{-6} and 8×10^{-5} C/cm², then the resist can be fully solubilized. Irradiation with fluxes greater than 8×10^{-5} C/cm² yields an insoluble spot after development.

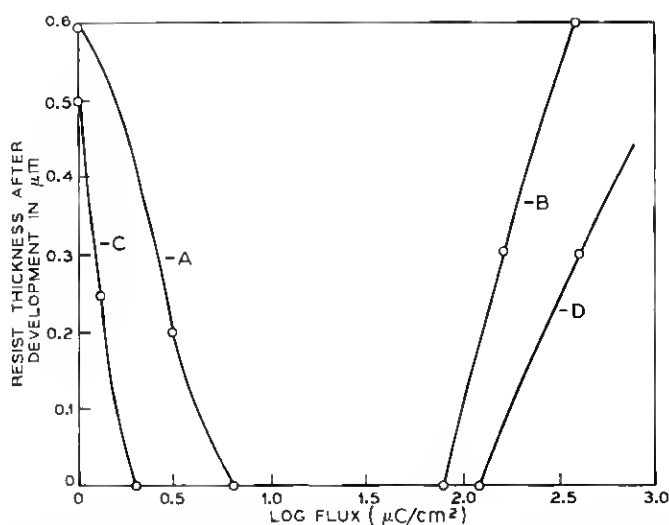


Fig. 2—Exposure of AZ-1350 by 15 keV electrons. Curves A and B newly purchased resist. Curves C and D, newly purchased AZ-1350 containing 2% benzotriazole. The initial thickness of resist was 0.6 μm .

The mechanisms of the reactions involved in the response of AZ-1350 to electron radiation have not been determined yet, but it is likely that a crosslinking reaction of its phenol-formaldehyde polymer^{2a} leads to the insoluble product. It is also likely that the solubilization reaction is the same one that occurs with light; quinone diazides are converted to carboxylic acids. Solubilization arising from a scission reaction of the phenol-formaldehyde polymer in which indiscriminate bond breakage occurs and soluble low molecular weight compounds result cannot be fully excluded, but it is not probably because scission would have to predominate at low exposures and crosslinking at high fluxes.

3.3 *Increasing the Sensitivity of AZ-1350 by the Addition of Benzotriazole*

When 2 percent solutions of benzotriazole in AZ-1350 are prepared, the flux of electrons needed to solubilize the resist is decreased (curve C, Fig. 2). Benzotriazole also inhibits crosslinking that occurs at high electron fluxes (curve D, Fig. 2). To date, the lowest fluxes required for full exposure are $2 \mu\text{C}/\text{cm}^2$.

Benzotriazole is not the only efficacious additive. All members of the benzotriazole, imidazole and indazole families that are soluble and that have a hydrogen atom bound to a nitrogen atom also decrease the flux needed to solubilize AZ-1350.

A full explanation for the effects of benzotriazole-type additives has not been developed yet, but crosslinking inhibition (curve D versus curve B, Fig. 2) probably arises from the antioxidant properties of benzotriazole; benzotriazole reacts with the free radicals generated by the absorption of energy before they cause crosslinking.

IV. INCREASED LIGHT SENSITIVITY OF PHOTORESISTS

Patterning semiconductor slices is conventionally done by contact exposure through a mask. In this process, a mask is placed on top of and in contact with a photoresist-coated slice and the photoresist exposed by ultraviolet light through the mask. In this way, a contact print of the mask is made on the photoresist. The lifetime of a mask copy is limited by abrasion of the mask during printing to about 10 exposures for an emulsion copy and about 150 exposures for a chrome copy. More important, contact with the mask results in defects, such as pinholes in the pattern and mechanical damage to the photoresist coated slice. Defects related to contact printing have been recognized

in the past, but their effect on the yield of discrete semiconductor devices is small. However, their effect on the yield of high precision, large area integrated circuits is much more severe.

An electron beam pattern generator writing on the sensitized resists discussed in the previous section offers one means of patterning silicon slices. Projection photolithography systems would benefit if more sensitive photoresists were available, since exposure times will be reduced and the problems of dust settling on the optics of the exposure system and the mechanical instabilities of the system would be minimized.

4.1 Increasing the Sensitivity of KPR to Light

Benzophenone and its derivatives have been reported to increase the sensitivity of polyvinyl cinnamate, the polymer in KPR, possibly because they increase the absorptivity of the system at longer wavelengths.²⁴ It was found here that benzophenone decreases the time required to produce the maximum thickness of KPR films (polyvinyl cinnamate and sensitizer) after development, but that the threshold flux is not decreased. (See Fig. 3.) This implies that the edge resolution of the image is increased, when benzophenone is present, and sharper etched lines should result. In neither this case nor in the

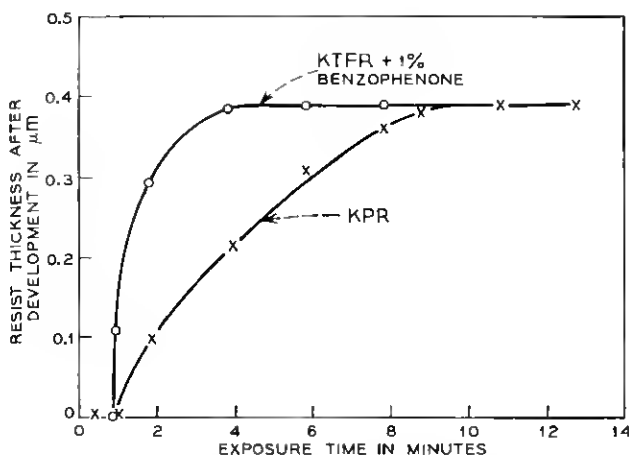


Fig. 3—Effect of benzophenone on the exposure of KPR by light. The source was a 150-W xenon lamp, 100 cm from the resist. The initial thickness of the resist was 0.6 μm .

case of the sensitization of AZ-1350 discussed below does the sensitization appear to arise from increased light absorption since the absorption spectra of the resists with and without additives are identical.

4.2 Increased Sensitivity of AZ-1350 to Light

The exposure time required to fully solubilize AZ-1350 can be reduced when low concentrations of benzotriazole or similar compounds are incorporated into the AZ-1350 film.²⁵ Some results are shown in Fig. 4.

V. SUMMARY

A photographic recording system suitable for use with a reticle generator has been developed. The electron flux required to fully expose negative photoresists has been reduced from 8–10 $\mu\text{C}/\text{cm}^2$ to 1.5 $\mu\text{C}/\text{cm}^2$ by incorporating additives into the resists. Other additives reduce the flux required to expose AZ-1350 from 6 $\mu\text{C}/\text{cm}^2$ to 2–3 $\mu\text{C}/\text{cm}^2$. Further reductions are anticipated for both systems.

Most of the additives that sensitize the response of resists to electrons also increase their sensitivity to light. So far, the photon flux required for full exposure has been reduced by a factor of 50 to 100 percent.

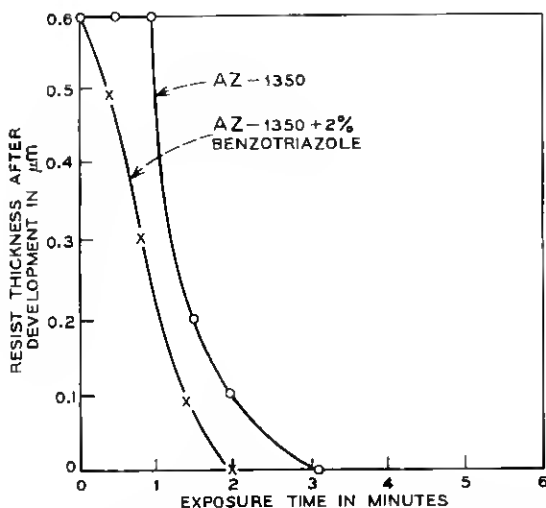


Fig. 4—Effect of benzotriazole on the exposure of AZ-1350 by a 150-W xenon lamp 100 cm from the sample. The initial thickness of the resist was 0.6 μm .

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REFERENCES

1. Samaroo, W. R., Raamot, J., and Parry, P. D., "An Electron Beam Pattern Generator," 1970 IEEE Convention Digest, New York, New York (March 1970).
2. Loeffler, K. H., "An Electron Beam System for Digital Recording," *Record of the Ninth Annual Symposium on Electron, Ion and Laser Beam Technology*, San Francisco: San Francisco Press, 1967, page 344.
3. Shepp, A., Whitney, R. E., and Masters, J. I., "Evaporated Silver Bromide as an Electron Beam Recording Material," *Photographic Sci. and Eng.*, **11** (September-October 1967), p. 322.
4. Broers, A. N., "Combined Electron and Ion Beam Processes for Microelectronics," *Microelectronics and Reliability*, **4**, No. 1 (January 1967), p. 103.
5. Kanya, K., Yamazaki, H., and Tanaka, K., "Measurement of Spot Size and Current Density Distribution of Electron Probes by Using Electron Beam Exposure of Kodak Photoresist Films," *Optik*, **25** (July 1967), p. 471.
6. Matta, R. K., "High Resolution Electron-Beam Exposure of Photoresists," *Electrochemical Technology*, **5**, No. 4 (July-August 1967), p. 382.
7. Broers, A. N., and Hatzakis, M., "Some New Characteristics of the Methacrylate Electron Resist," 10th Symposium on Electron, Ion and Laser Beam Technology, Gaithersburg, Maryland, May 1969.
8. Roberts, E. E., "Rapid Direct Deposition of Siliceous Diffusion Barriers by Electron Beams," 133rd Meeting Electrochem. Soc., Boston, Massachusetts, May 1968.
9. Yatsui, Y., Nakata, T., and Umehara, K., "Electron Beam Exposure of Silicones," *J. Electrochem. Soc.*, **116**, No. 1 (1969), p. 97.
10. Pease, R. F. W., and Nixon, W. C., "Microformation of Filaments," *First Inter. Conf. on Electron and Ion Beams*, R. Bakish, Editor, New York: John Wiley, 1964, p. 250.
11. Hansen, J. R., and Schneeberger, J. R., "Liquid Crystal Media for Electron Beam Recording," Paper 15.1, IEEE Electron Devices Meeting, Washington, D. C., 1967.
12. Blanchard, J. G., and Hart, D. M., "Electron Beam Recording and Readout," *IBM Technical Disclosures*, **9**, No. 5 (May 1967), p. 1762.
13. Land, C. E., "Ferroelectric Ceramic Electro-Optic Storage and Display Devices," Paper 15.2, IEEE Electron Devices Meeting, Washington, D. C., 1967.
14. Clenn, W. E., Jr., "Thermoplastic Recording," *J. Appl. Phys.*, **30**, No. 12 (December 1959), pp. 1870-1873.
15. Krittman, I. W., and Inslee, J. W., "Discussion and Applications of Electrostatic Signal Recording," *RCA Rev.*, **24**, No. 3 (September 1963), p. 406.
16. Tarnowski, A. A., and Evans, C. H., "Photographic Data Recording by Direct Exposure With Electrons," *J. Soc. Motion Picture and Television Engineers*, **71**, No. 10 (October 1962), p. 765.
17. Kosar, J., *Light Sensitive Systems*, New York: John Wiley, 1965.
18. Brojde, B., "Exposure of Photoresists: Electron Exposure of Negative Photoresists," *J. Electrochem. Soc.*, **116**, No. 9 (September 1969), p. 1241.
19. Levine, H. A., "Positive Photoresist Materials," *Polymer Preprints*, Amer. Chem. Soc., **10** (January 1969), p. 337.
20. Brojde, B., "Electron Beam Exposure of Sensitized Photoresists," 134th Meeting, Electrochem. Soc., Montreal, Quebec, October 1968.

21. Kikuchi, S., and Nakamura, K., *The Photocrosslinking of Polyvinyl Cinnamate, Postprints of Photopolymers—Principles, Processes, and Materials*, New York: Soc. Plastics Eng., 1967, p. 175.
22. Moreau, W. M., "Photosensitization of Polyvinyl Cinnamate," *Polymer Preprints*, Amer. Chem. Soc., 10 (January 1969), p. 362.
23. Harwood, M. G., and Hunter, D. N., "A Study of Some Photosensitive Resists Used in Microcircuitry," AD 846, 184.
24. Minsk, L. M., Van Deusen, W. P., and Robertson, E. M., "Photosensitization of Polymeric Cinnamic Acid Esters," U. S. Patent 2,670,287, applied for January 20, 1961, issued February 23, 1954.
25. Broyde, B., "Exposure of Photoresists: II. Electron and Light Exposure of a Positive Photoresist," 137 Meeting, Electrochem. Soc., Los Angeles, California, May 1970.